Electronic Supplementary Material (ESI) for Green Chemistry

Supporting information

Cyclization of o-Phenylenediamines by CO_2 in the presence of H_2 to the Synthesis of Benzimidazoles

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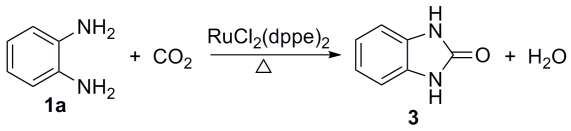
This file includes:

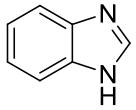
1. Procedure for the synthesis of byproduct from *o*-phenylenediamine and CO_2:



o-Phenylenediamines (5.0 mmol) was loaded into a Teflon-lined stainless steel reactor of 22 mL coupled with a magnetic stirrer. The reactor was sealed and maintained at 120 °C in an oil bath, which was controlled by a Haake-D3 temperature controller. Then CO_2 was charged into the reactor up to 15 MPa, and the stirrer started. After 40 h, the reactor was cooled in ice water and the gas inside was slowly released. The separation process of the reaction mixture was similar to that mentioned above. The results showed that 2-benzimidazolone was the sole product. The isolated product was identified by ^{1}H and ^{13}C NMR.

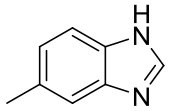
2. ^{1}H and ^{13}C NMR data of the as-synthesized products:

2a: Benzimidazole



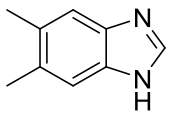
The above compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent to afford the product in 92% yield (0.546 g, 4.64 mmol). The characterization data obtained for benzimidazole were identical to those previously reported in the literature [1]. ^{1}H NMR (400 MHz, DMSO, 293 k): δ 12.44 (s, 1H), 8.21 (s, 1H), 7.58 (dd, J = 5.9, J = 3.2 Hz, 2H), 7.29 – 7.07 (m, 2H); ^{13}C NMR (100 MHz, DMSO, 293 k): δ 141.9 (CH), 138.0 (C), 121.7 (CH), 115.3 (CH).

2b: 5-methylbenzimidazole



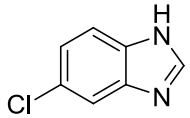
The above compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent to afford the product in 95% yield (0. 627 g, 4.75 mmol). The characterization data obtained for 5-methylbenzimidazole were identical to those previously reported in the literature [1]. ^{1}H NMR (400 MHz, DMSO) δ 12.30 (s, 1H), 8.12 (s, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.36 (s, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4 (CH), 136.4 (C), 135.4 (C), 131.8 (C), 123.4 (CH), 114.5 (CH), 113.8 (CH), 20.7 (CH_3).

2c: 5, 6-Dimethylbenzimidazole



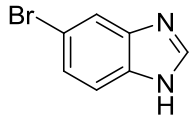
The above compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent to afford the product in 93% yield (0.679 g, 4.65 mmol). The characterization data obtained for 5, 6-dimethylbenzimidazole were identical to those previously reported in the literature [2]. ^{1}H NMR (400 MHz, DMSO) δ 12.23 (s, 1H), 8.07 (s, 1H), 7.36 (s, 2H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 140.51 (C), 136.20 (CH), 129.61 (CH), 114.81 (CH), 19.44 (CH_3).

2d: 5-chlorobenzimidazole



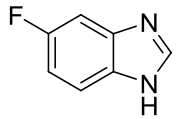
The above compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent to afford the product in 91% yield (0.691 g, 4.55 mmol). The characterization data obtained for 5-chlorobenzimidazole were identical to those previously reported in the literature [2]. ^{1}H NMR (400 MHz, DMSO) δ 12.61 (s, 1H), 8.27 (s, 1H), 7.65 (s, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.21 (dd, *J* = 8.5, J = 1.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 143.4 (CH), 139.3 (C), 136.6 (C), 126.2 (C), 122.0 (CH), 116.4 (CH), 115.2 (CH).

2e: 5-Bromobenzimidazole



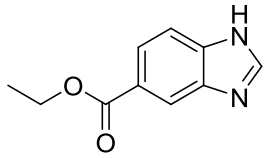
The above compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent to afford the product in 90% yield (0.886 g, 4.50 mmol). The characterization data obtained for 5-bromobenzimidazole were identical to those previously reported in the literature [3]. ^{1}H NMR (400 MHz, DMSO) δ 12.70 (s, 1H), 8.31 (s, 1H), 7.83 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 142.80 (C), 124.17 (CH), 113.62 (CH).

2f: 5-Fluorobenzimidazole



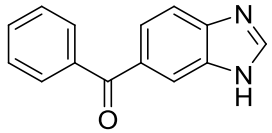
The above compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent to afford the product in 91% yield (0.619 g, 4.55 mmol). The characterization data obtained for 5-fluorobenzimidazole were identical to those previously reported in the literature [4]. ^{1}H NMR (400 MHz, DMSO) δ 12.81 (s, 1H), 8.38 (s, 1H), 7.63 (dd, *J* = 8.5, 4.9 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.04 (td, *J* = 9.7, 1.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 158.29 (C), 143.01 (C), 140.79 (CH), 134.60 (CH), 115.70 (CH), 109.62 (CH), 100.93 (CH).

2g: Etheyl benzimidazole-5-carboxylate



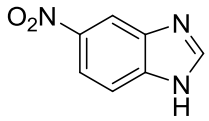
The above compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent to afford the product in 93% yield (0.883 g, 4.65 mmol). Melting point : 135-136 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.73 (s, 1H), 8.43 (s, 1H), 8.24 (s, 1H), 7.84 (dd, *J* = 8.5, *J* = 1.3 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 166.5 (C), 144.8 (C), 141.2 (CH), 138.4 (C), 123.8 (CH), 123.2 (CH), 117.8 (CH), 115.1 (CH), 60.7 (CH_2), 14.5 (CH_3). FTIR (KBr): 3089, 2983, 2801,1710, 1624, 1582, 1520,1475, 1414, 1367, 1305, 1232, 1123, 956, 892, 887,776,753 cm^{-1}. HRMS (EI): calcd. for $C_{10}H_{10}N_2O_2^+$ [M^+] 190.0742, found 190.0740.

2h: 5-Benzoylbenzimidazole



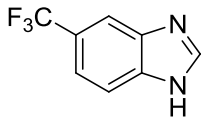
The above compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent to afford the product in 92% yield (1. 021 g, 4.60 mmol). The characterization data obtained for 5-benzoylbenzimidazole were identical to those previously reported in the literature [1]. ^{1}H NMR (400 MHz, DMSO) δ 12.91 (s, 1H), 8.49 (s, 1H), 8.04 (s, 1H), 7.83 – 7.65 (m, 4H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 195.34 (CO), 155.18 (C), 144.37 (C), 137.73 (C), 133.67 (C), 131.51 (C), 130.49 (CH), 129.02 (CH), 127.88 (CH), 123.41 (CH), 109.43 (CH), 107.55 (CH).

2i: 5-Nitrobenzimidazole



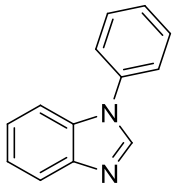
The above compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent to afford the product in 87% yield (0.709 g, 4.35 mmol). The characterization data obtained for 5-nitrobenzimidazole were identical to those previously reported in the literature [2]. ^{1}H NMR (400 MHz, DMSO) δ 8.38 (s, 1H), 8.51 (d, *J* = 2.1 Hz, 1H), 8.11 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 146.26 (C), 142.15 (C), 117.10 (CH).

2j: 5-Trifluoromethylbenzimidazole



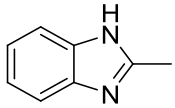
The above compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent to afford the product in 73% yield (0.679 g, 3. 65 mmol). The characterization data obtained for 5-trifluoromethylbenzimidazo -le were identical to those previously reported in the literature [5]. ^{1}H NMR (400 MHz, DMSO) δ 12.89 (s, 1H), 8.45 (s, 1H), 7.97 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.49 (dd, *J* = 8.5, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 144.27 (C), 128.67 (CF_3), 125.97 (CF_3), 123.27 (CF_3), 122.27 (CH), 121.95 (CH), 120.57 (CF_3), 118.03 (CH).

2k: N-Phenylbenzimidazole



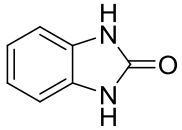
The above compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent to afford the product in 92% yield (0.892 g, 4.60 mmol). The characterization data obtained for N-phenylbenzimidazole were identical to those previously reported in the literature [6]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.94 – 7.86 (m, 1H), 7.62 – 7.44 (m, 6H), 7.35 (dd, *J* = 9.1, *J* =5.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7 (C), 135.3 (CH), 132.7 (C), 129.1 (CH), 127.1 (CH), 123.1 (CH), 122.8 (CH), 121.9 (CH), 119.5 (CH), 109.5 (CH).

2l: 2-Methyl-1H-benzimidazole



The above compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent to afford the product in 98% yield (0.646 g, 4.90 mmol). The characterization data obtained for 2-Methyl-1H-benzimidazole were identical to those previously reported in the literature [7]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.0, *J* = 3.2 Hz, 2H), 7.22 (dd, *J* = 6.0, *J* = 3.2 Hz, 2H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7 (C), 139.1 (C), 122.6 (CH), 114.9 (CH), 15.41 (CH_3).

3: 2-Benzimidazolone



The characterization data obtained for 2-benzimidazolone were identical to those previously reported in the literature [8]. ^{1}H NMR (400 MHz, DMSO, 293 k): δ 10.49 (s, 2H), 6.81 (s, 4H); ^{13}C NMR (100 MHz, DMSO, 293 k): δ 155.7 (C), 130.1 (C), 120.8 (CH), 108.9 (CH).

3. Copies of the ^{1}H and ^{13}C NMR spectra (Figures S1-S26)

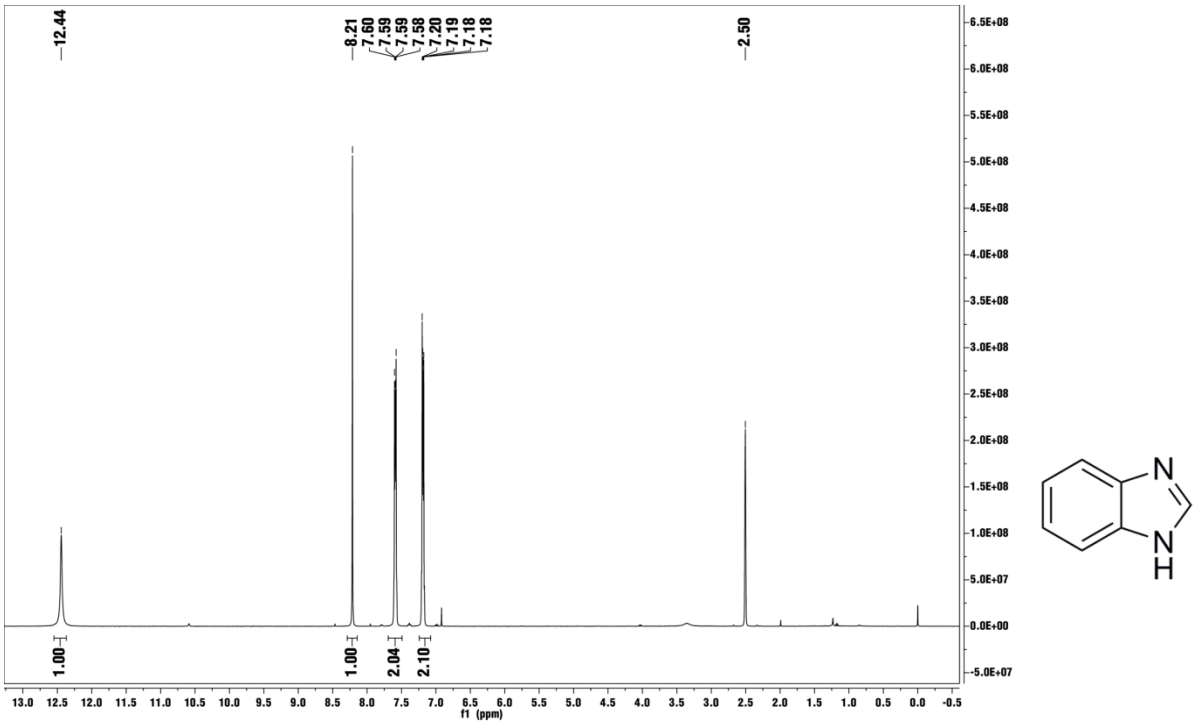


Figure S1. ^{1}H NMR Spectra of 1H-Benzimidazole (2a)

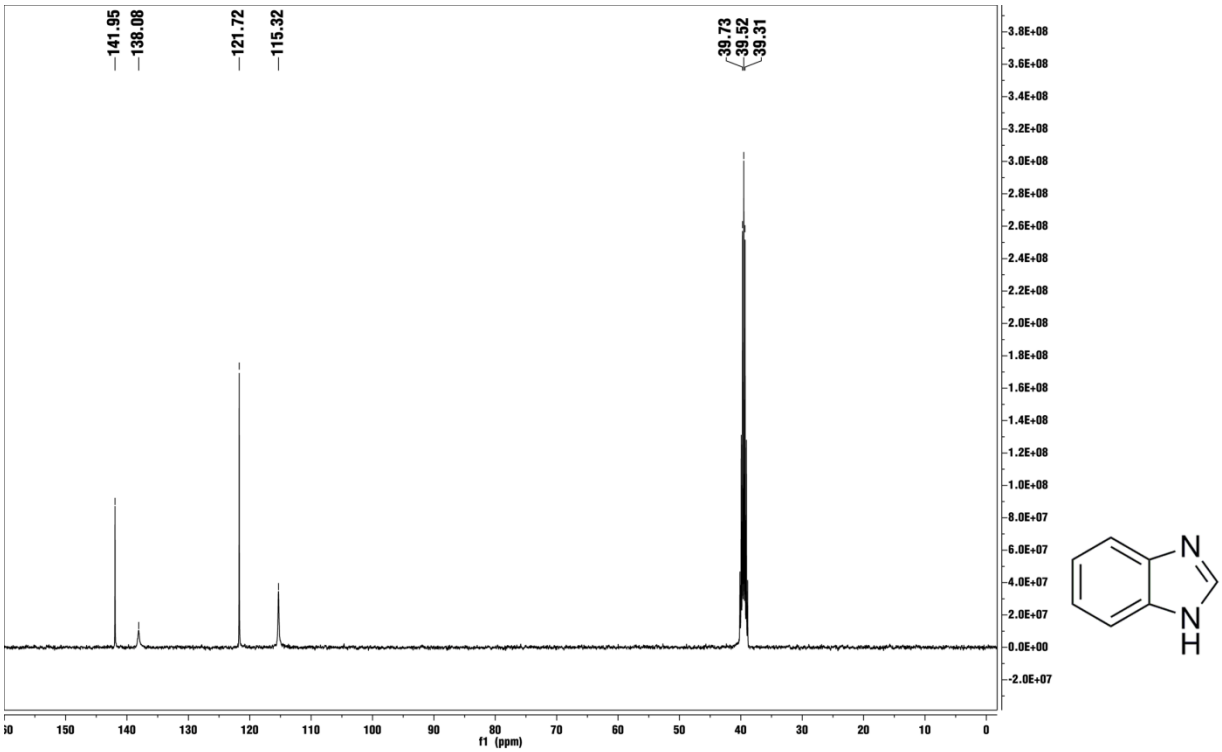


Figure S2. ^{13}C NMR Spectra of 1H-Benzimidazole (2a)

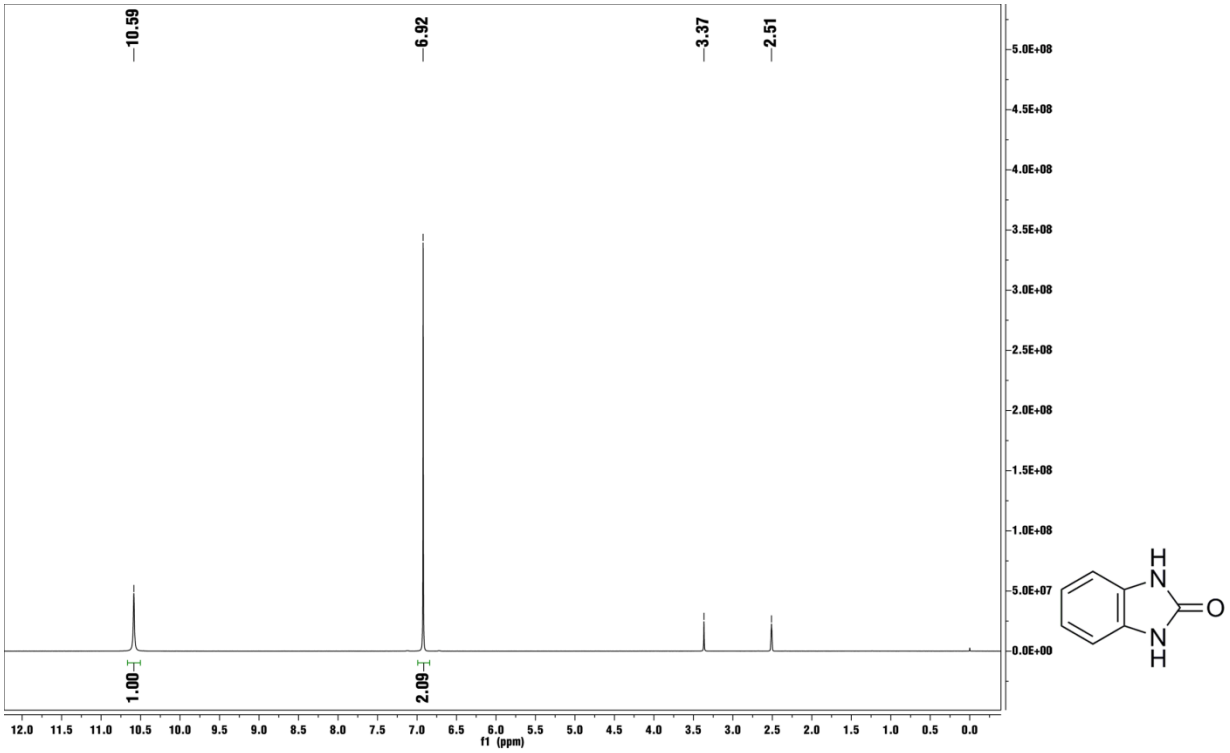


Figure S3. ^{1}H NMR Spectra of 2-Benzimidazolinone (3)

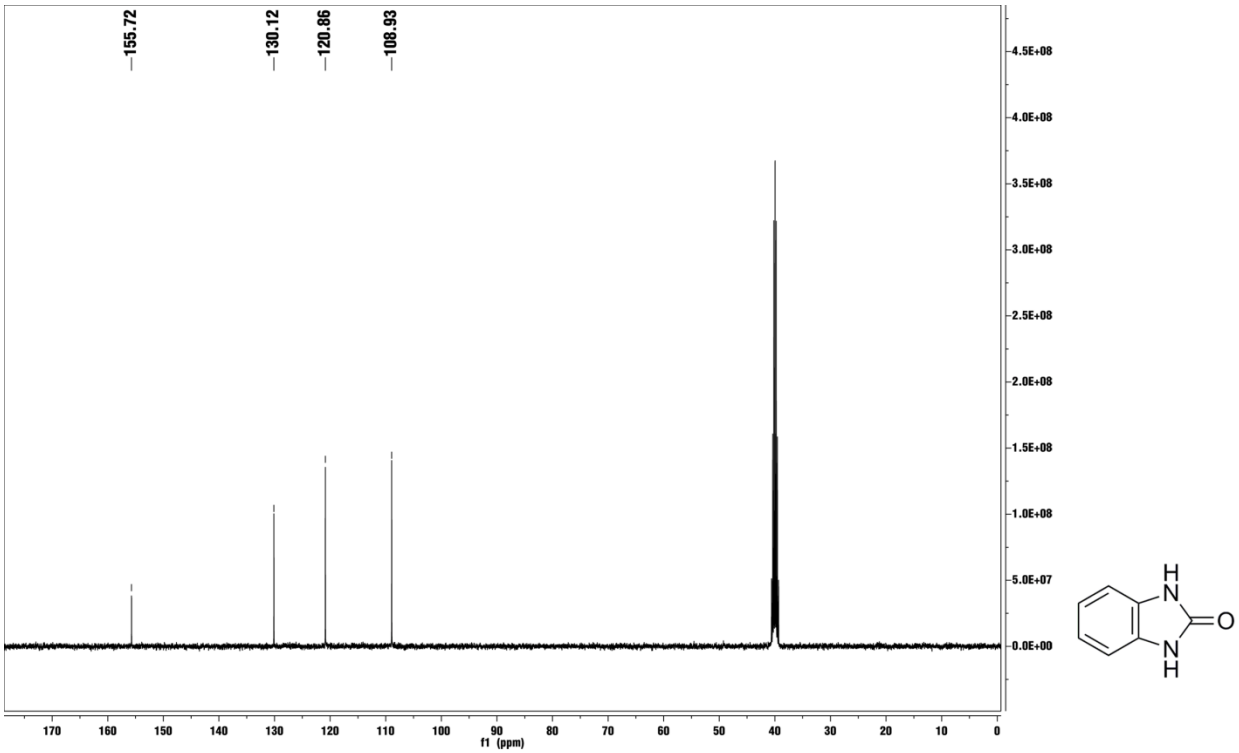


Figure S4. ^{13}C NMR Spectra of 2-Benzimidazolinone (3)

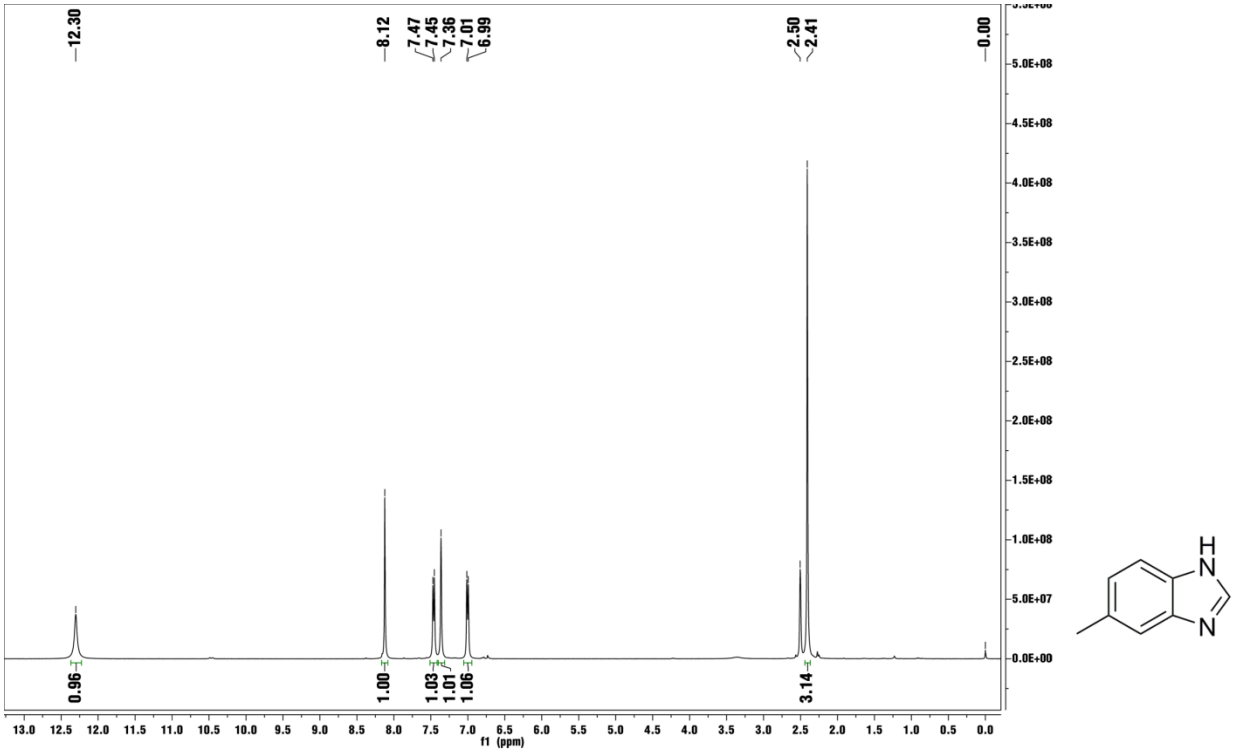


Figure S5. ^{1}H NMR Spectra of 5-methyl-benzimidazole (2b)

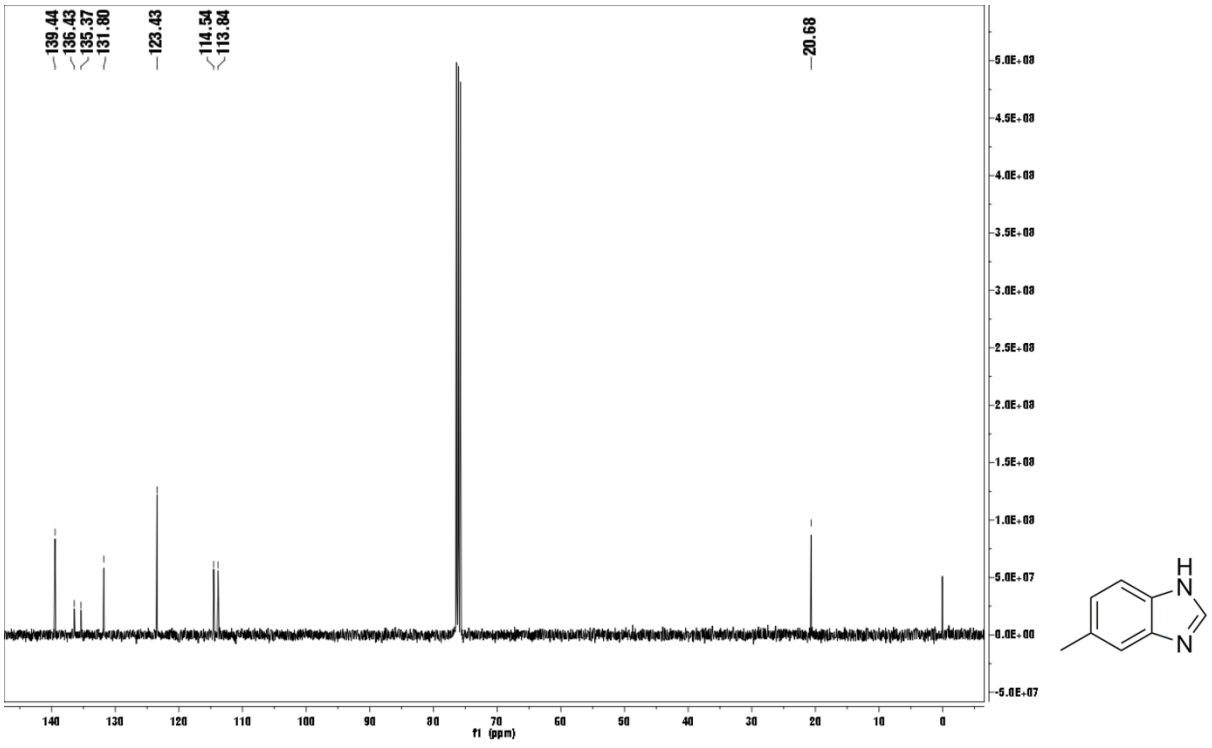


Figure S6. ^{13}C NMR Spectra of 5-methyl-benzimidazole (2b)

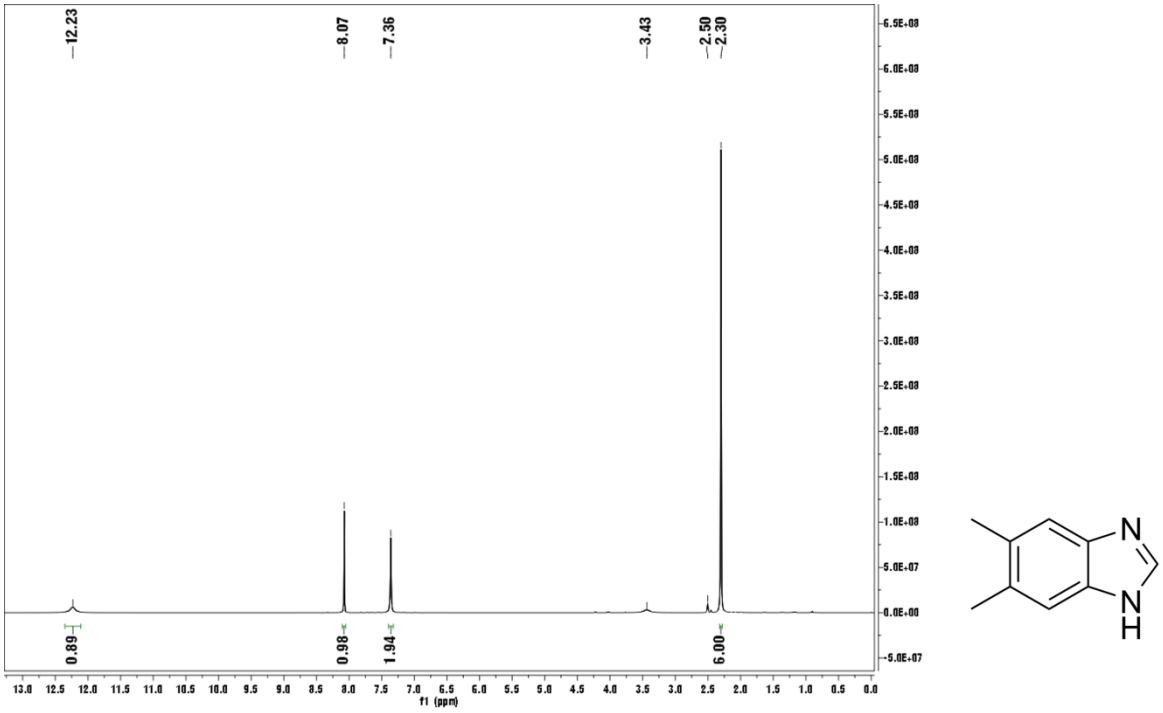


Figure S17. ^{1}H NMR Spectra of 5,6-dimethylbenzimidazole (2c)

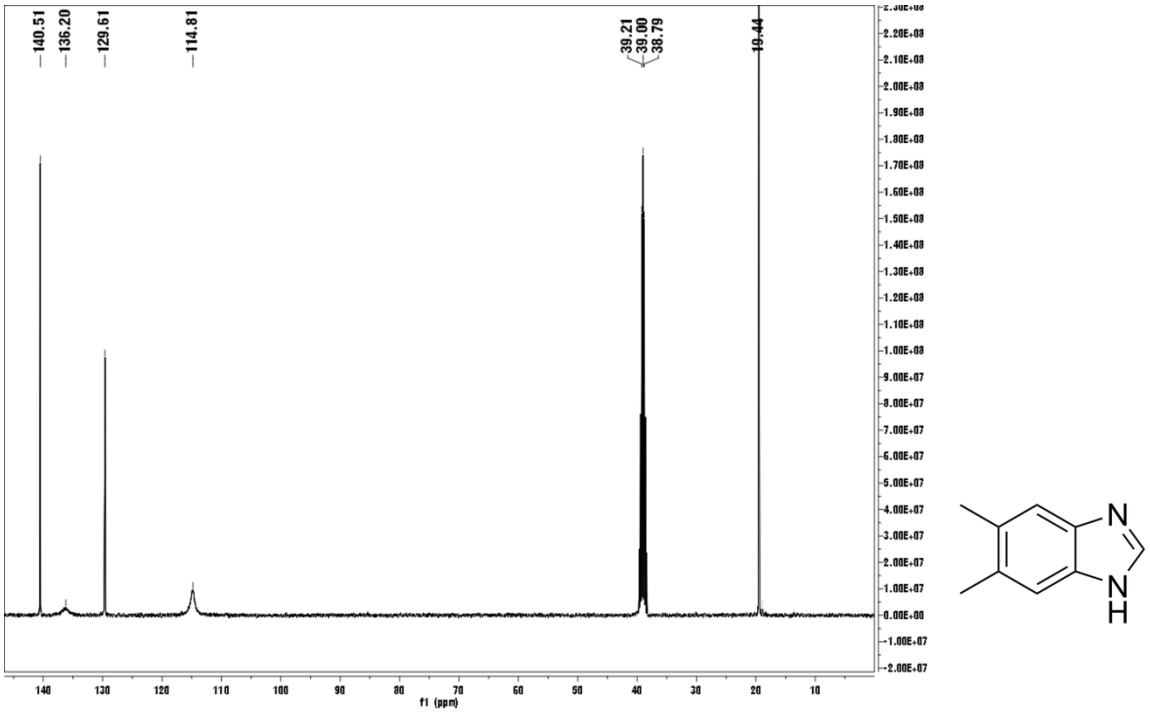


Figure S18. ^{13}C NMR Spectra of 5,6-dimethylbenzimidazole (2c)

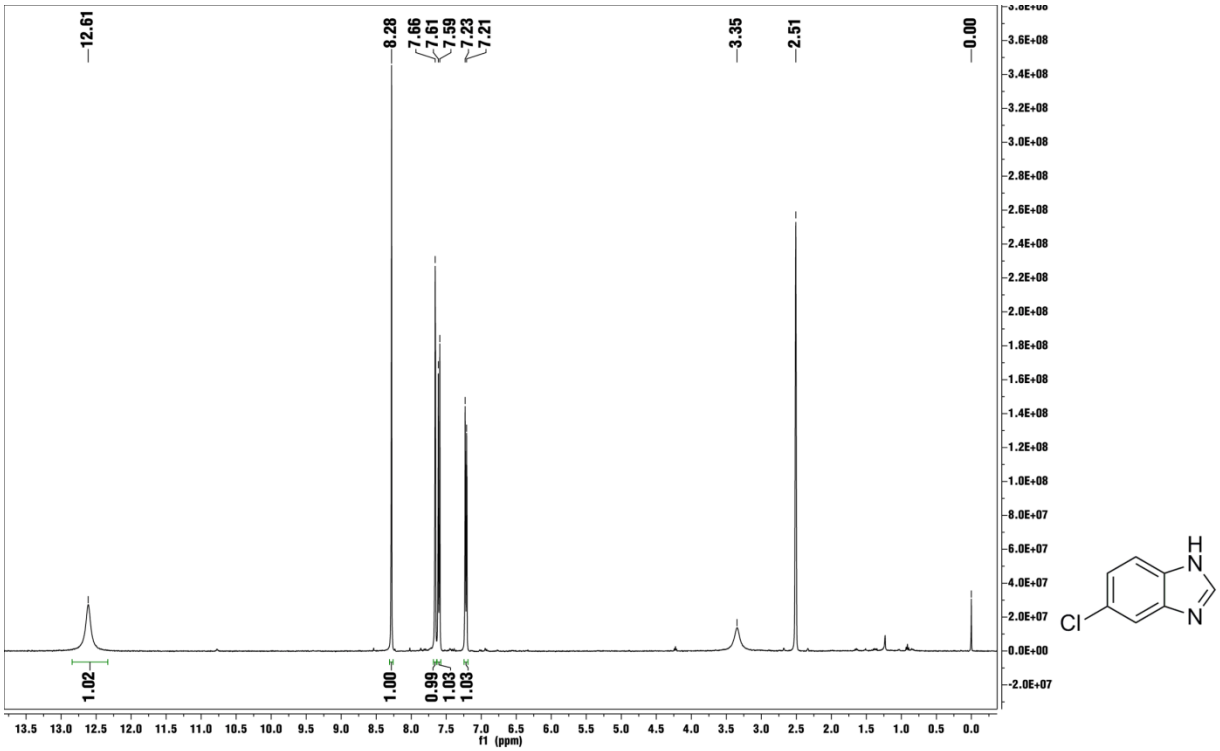


Figure S7. ^{1}H NMR Spectra of 5-chlorobenzimidazole (2d)

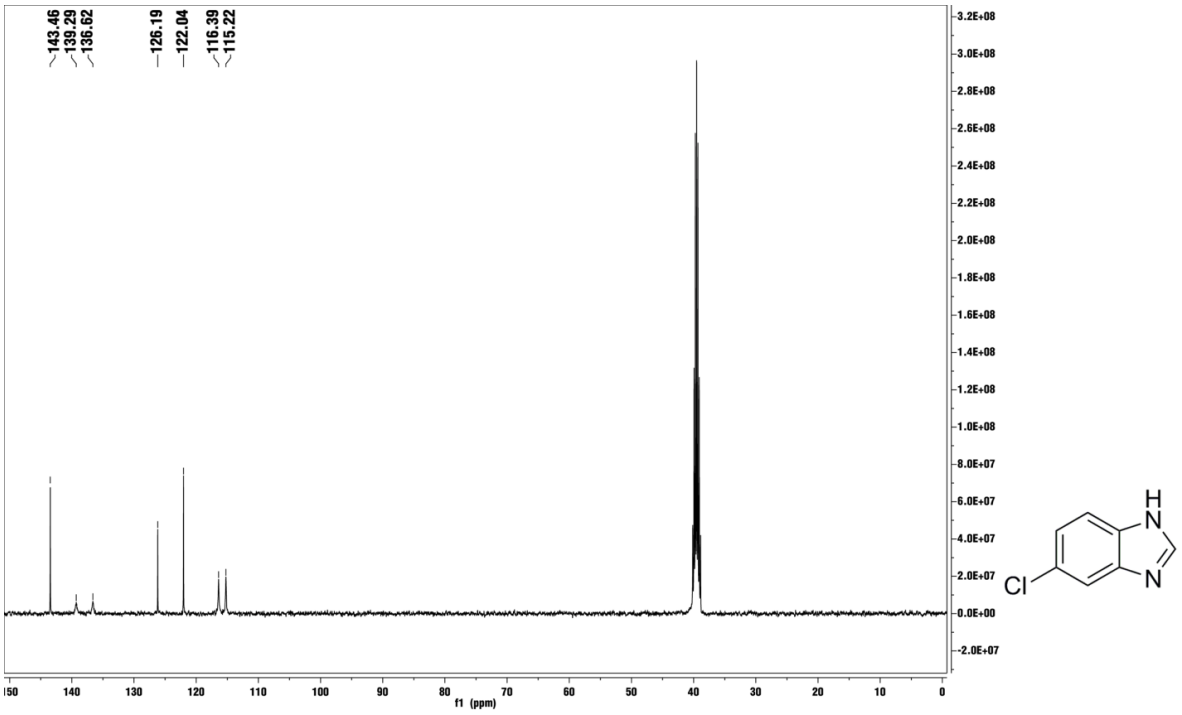


Figure S8. ^{13}C NMR Spectra of 5-chlorobenzimidazole (2d)

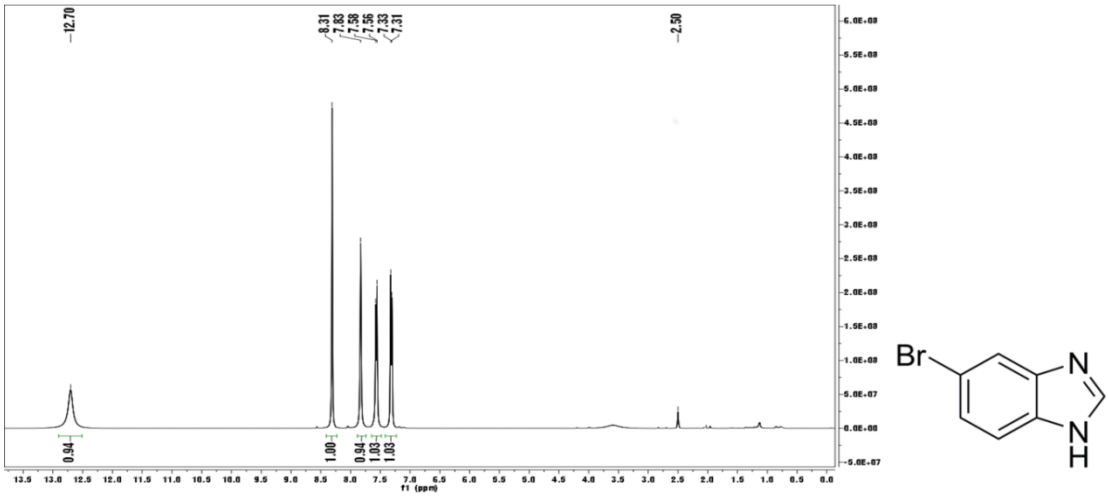


Figure S13. ^{1}H NMR Spectra of 5-bromobenzimidazole

(2e)

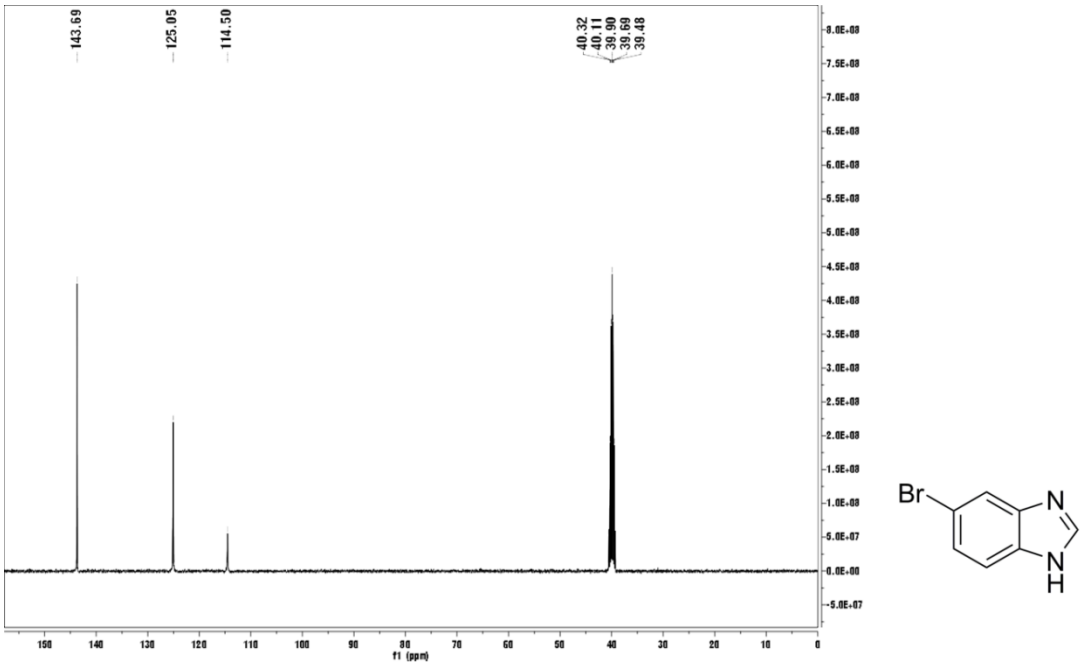
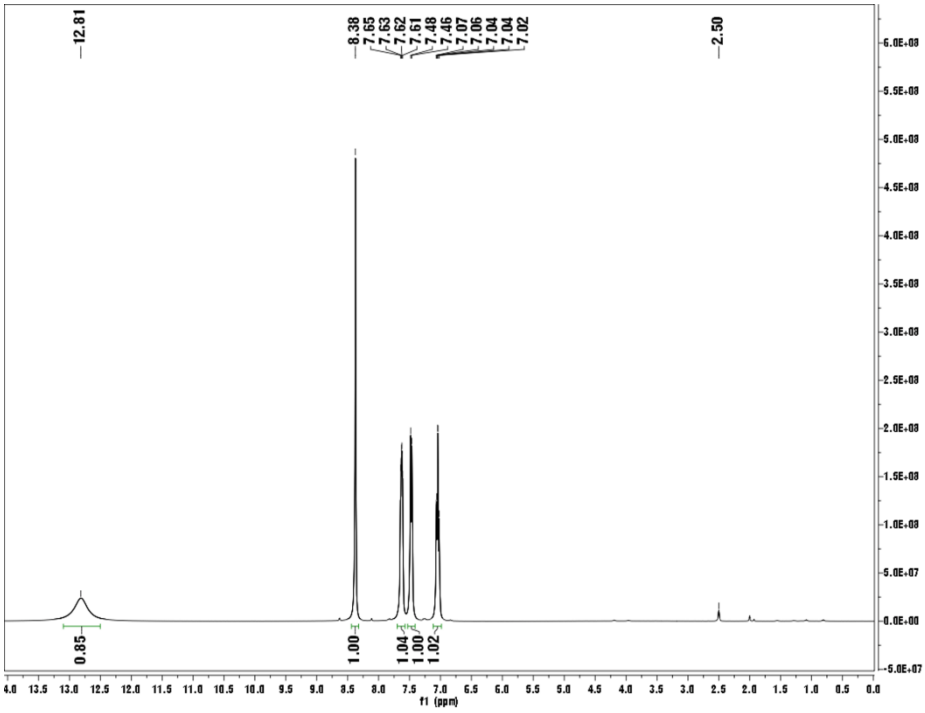


Figure S14. ^{13}C NMR Spectra of 5-bromobenzimidazole (2e)



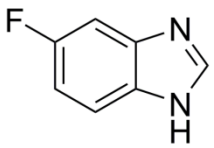
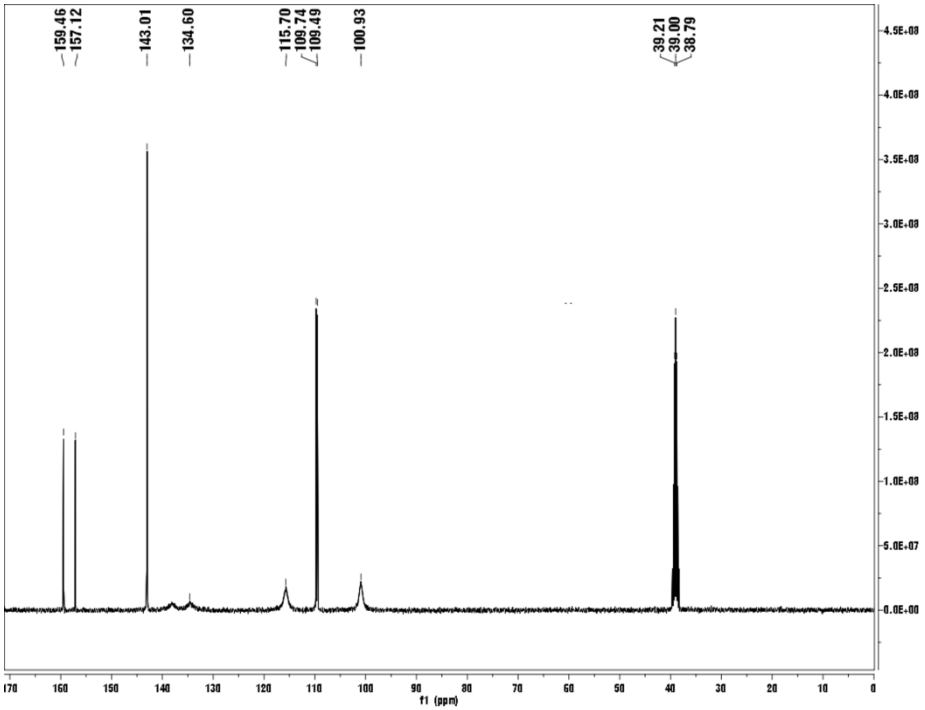


Figure S15. ^{1}H NMR Spectra of 5-fluorobenzimidazole (2f)



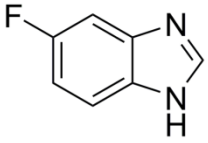


Figure S16. ^{13}C NMR Spectra of 5-fluorobenzimidazole (2f)

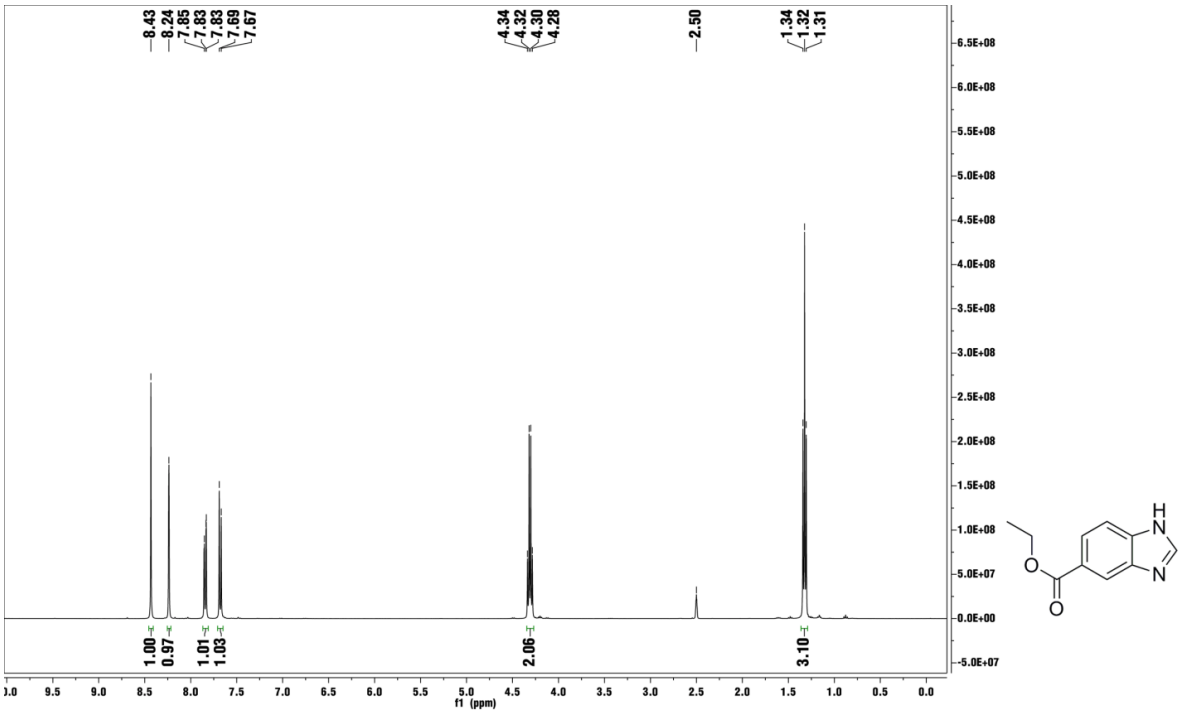


Figure S9. ^{1}H NMR Spectra of Etheyl benzimdiazole-5-carboxylate (2g)

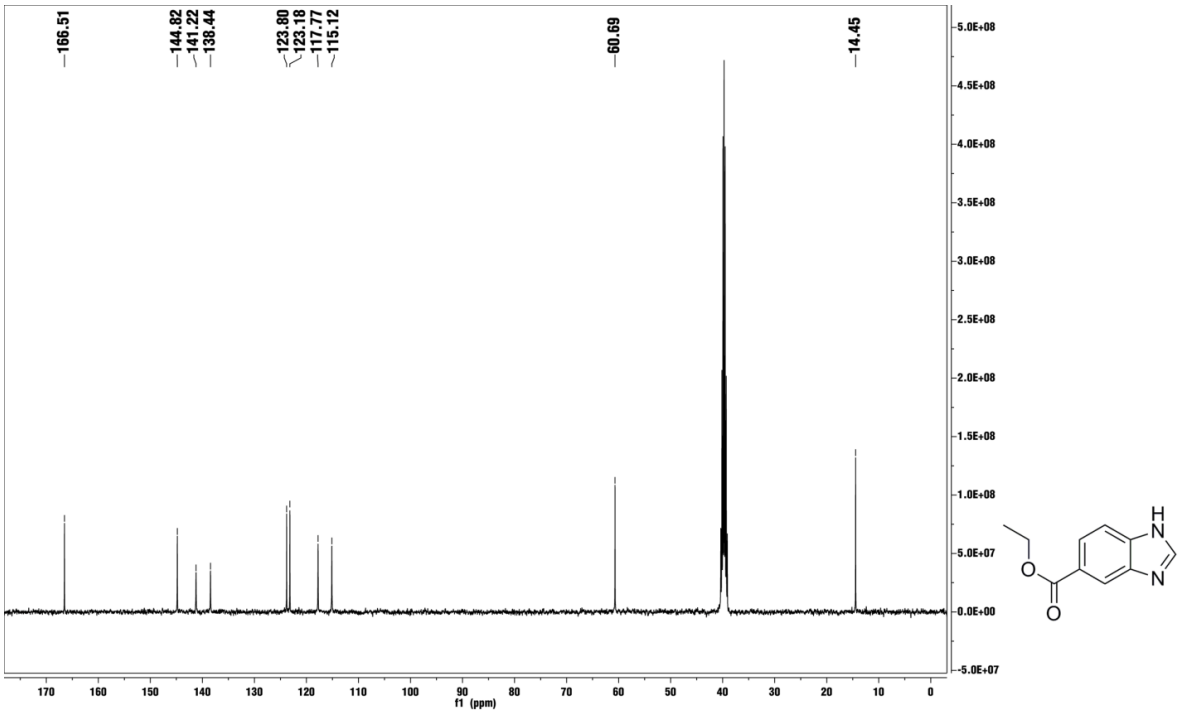


Figure S10. ^{13}C NMR Spectra of Etheyl benzimidazole-5-carboxylate (2g)

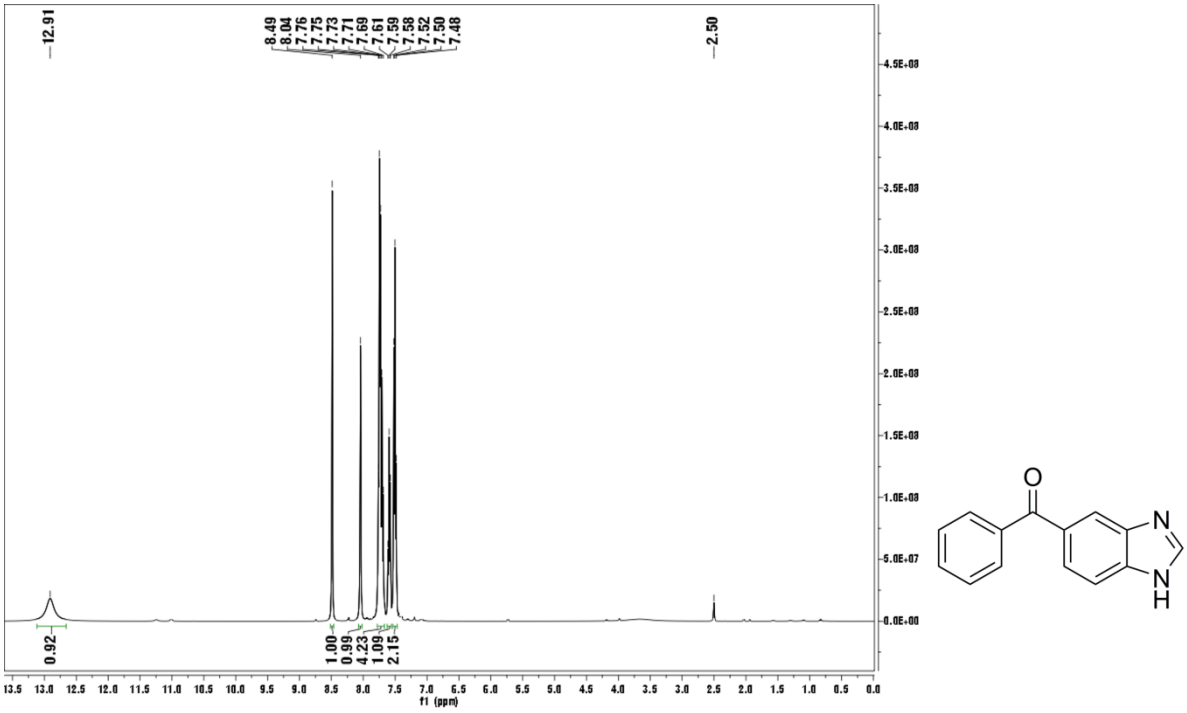


Figure S19. ^{1}H NMR Spectra of 5-benzoylbenzimidazole (2h)

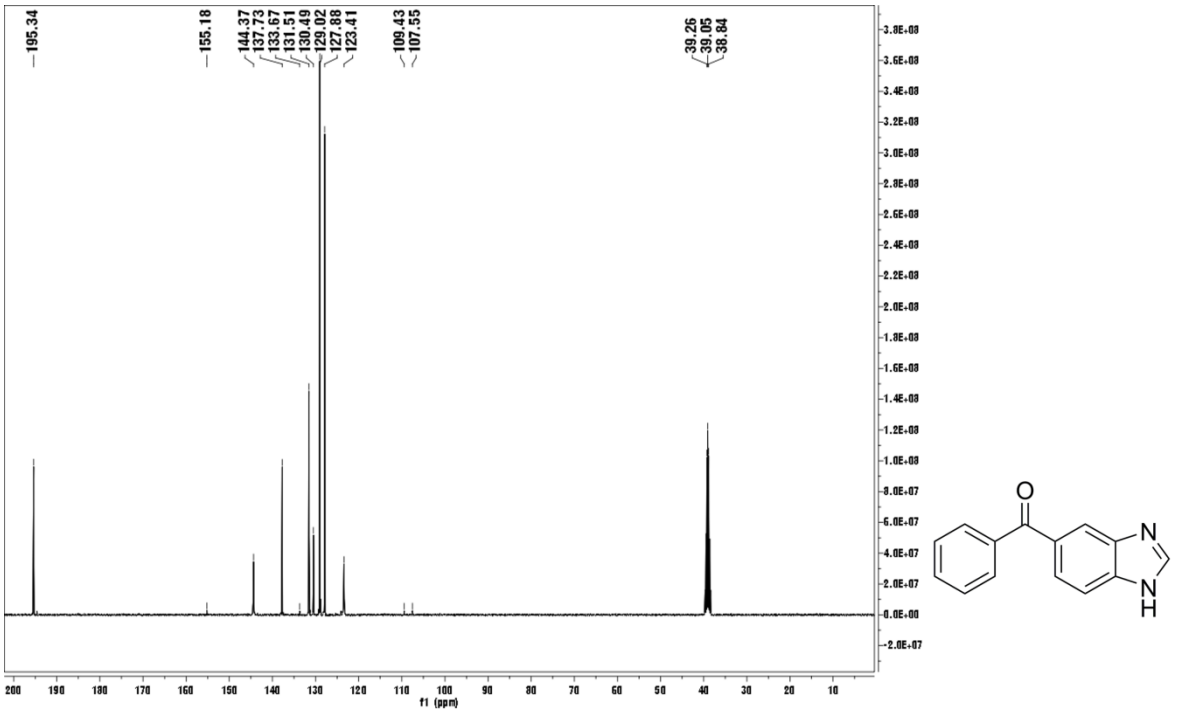


Figure S20. ^{13}C NMR Spectra of 5-benzoylbenzimidazole (2h)

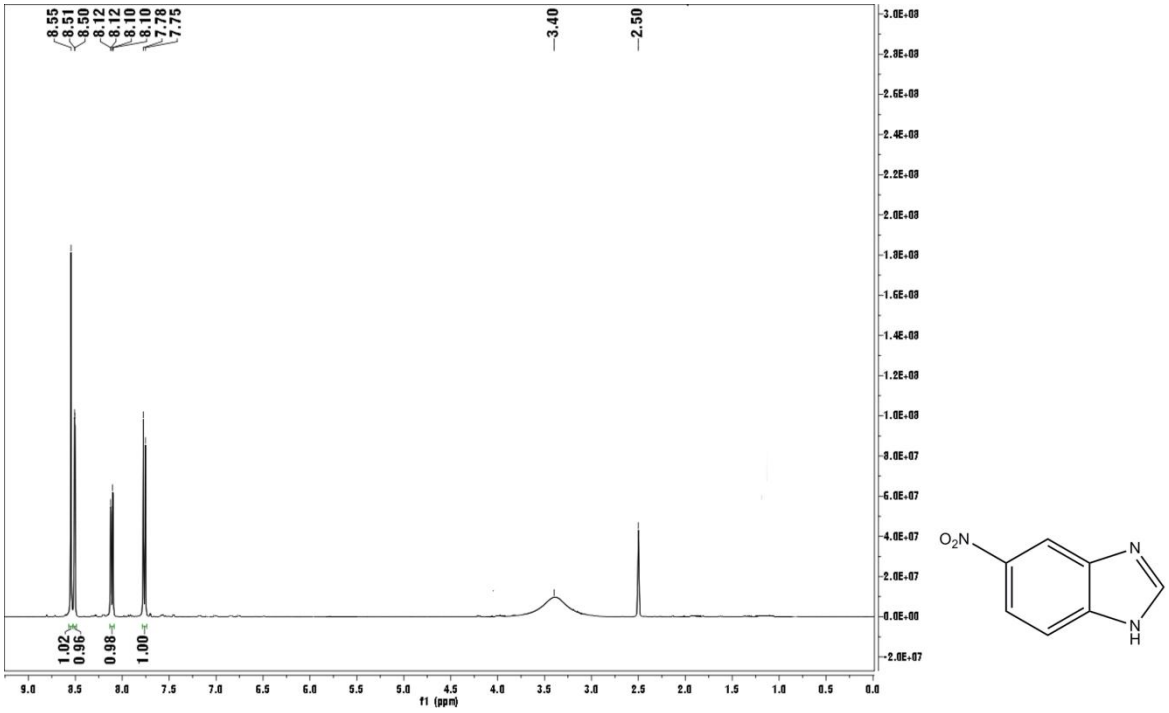


Figure S23. ^{1}H NMR Spectra of 5-nitrobenzimidazole (2i)

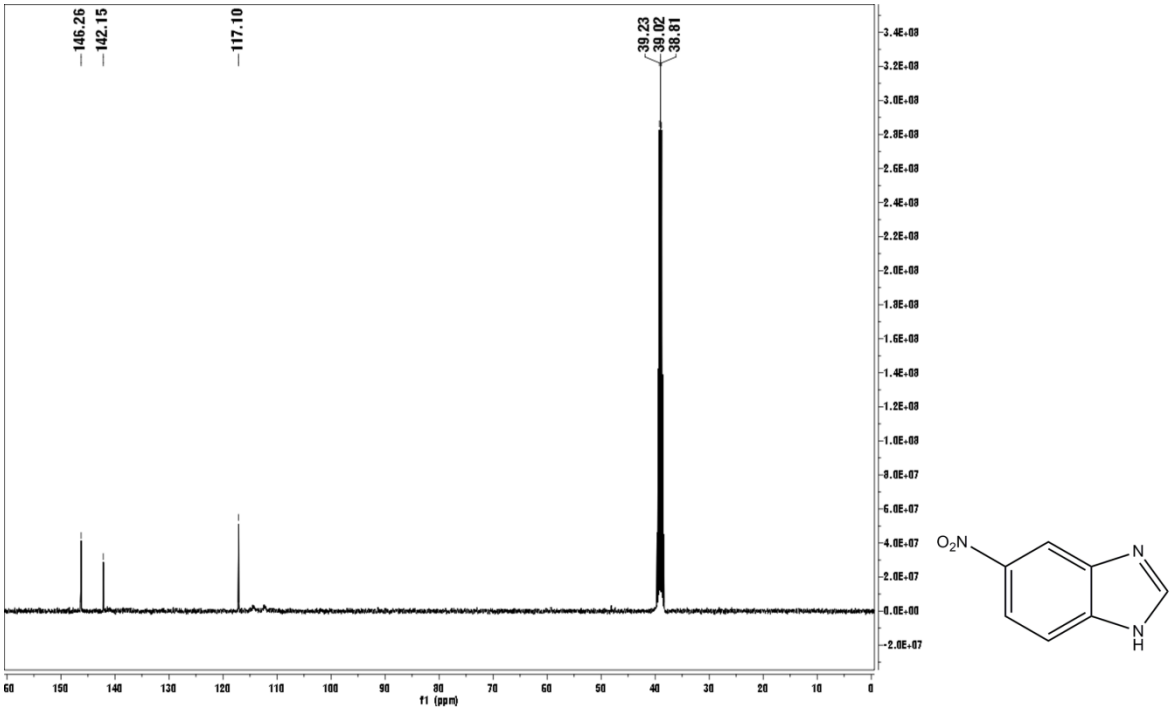


Figure S24. ^{13}C NMR Spectra of 5-nitrobenzimidazole (2i)

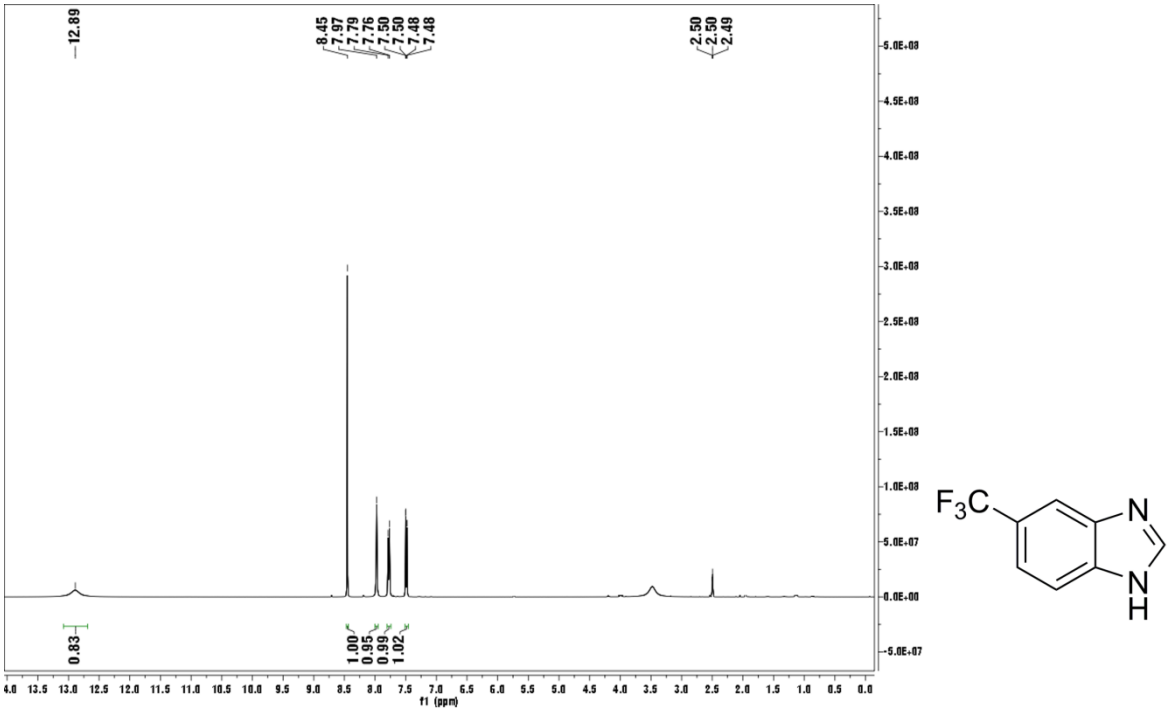


Figure S21. ^{1}H NMR Spectra of 5-trifluoromethylbenzimidazole (2j)

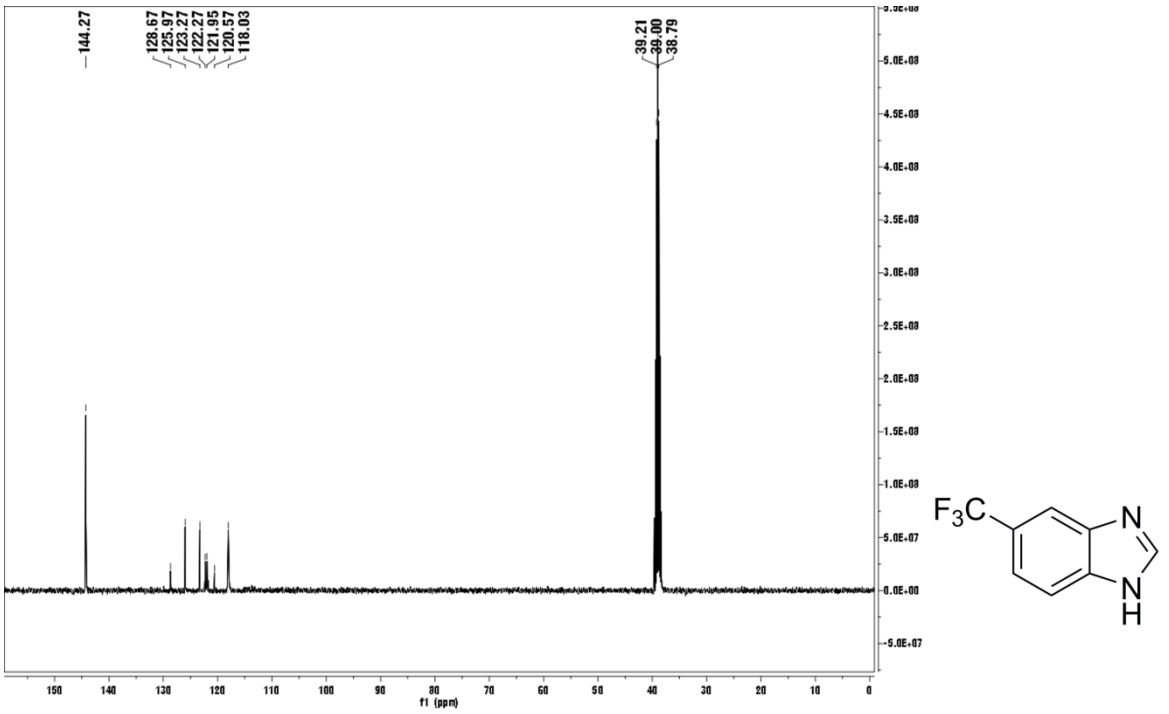


Figure S22. ^{13}C NMR Spectra of 5-trifluoromethylbenzimidazole (2j)

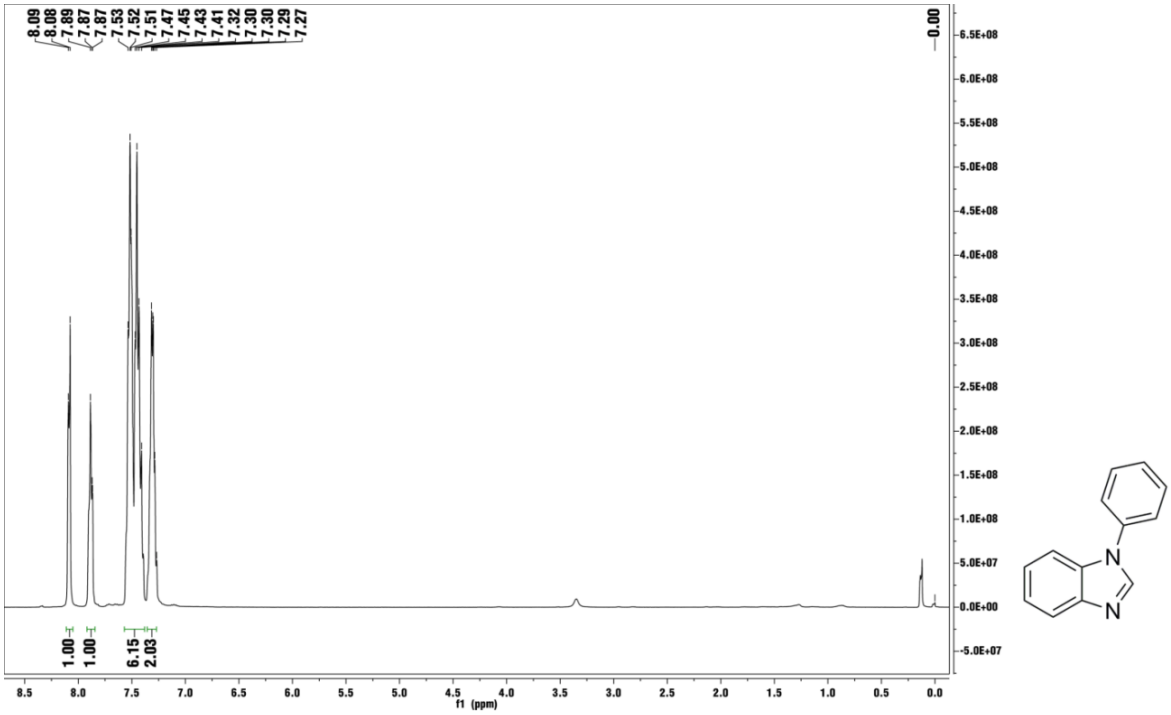


Figure S11. ^{1}H NMR Spectra of N-phenyl-1H-benzimidazole (2k)

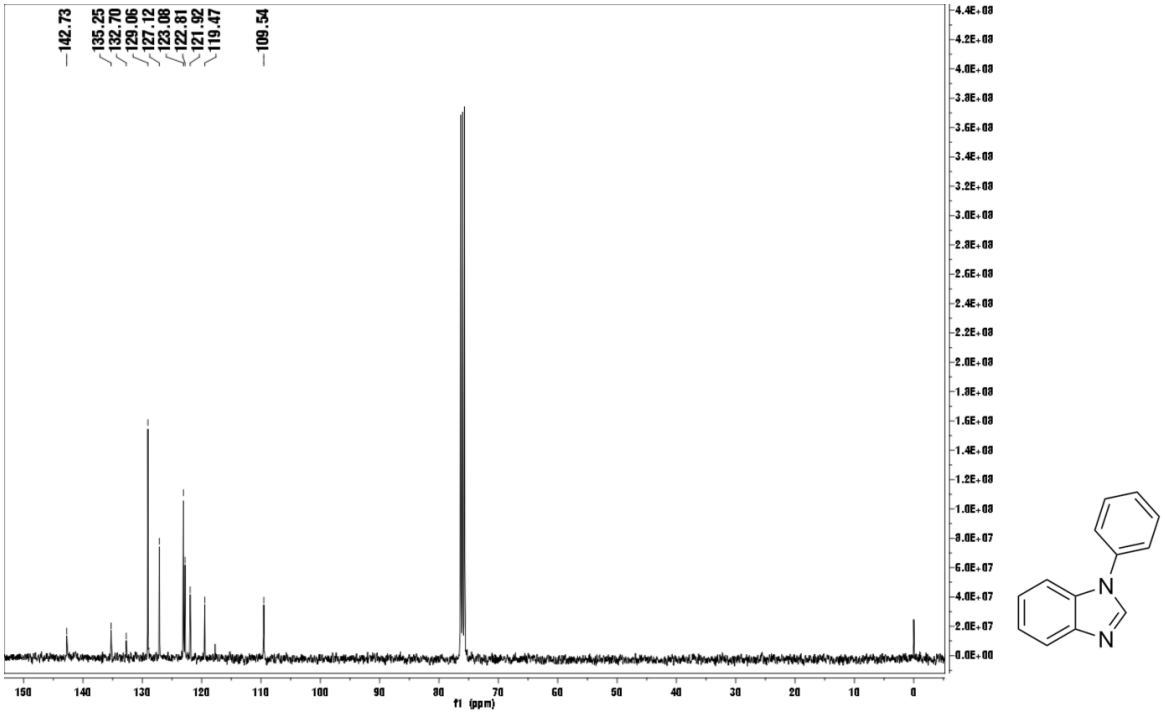


Figure S12. ^{13}C NMR Spectra of N-phenyl-1H-benzimidazole (2k)

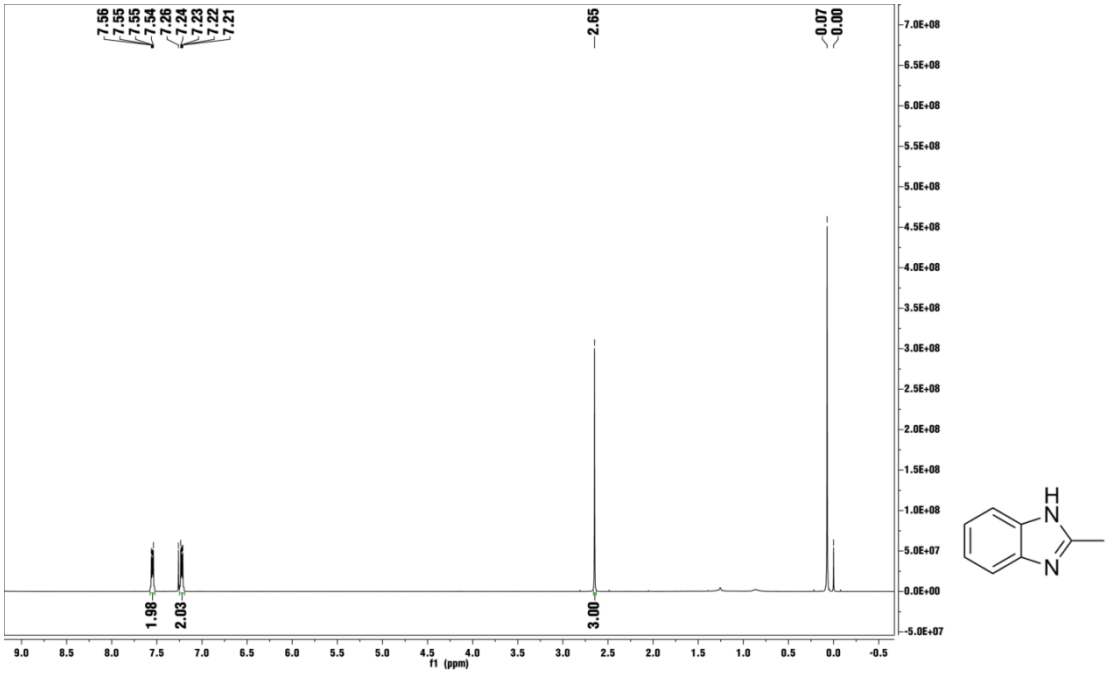


Figure S25. ^{1}H NMR Spectra of 2-Methyl-1H-benzimidazole (2l)

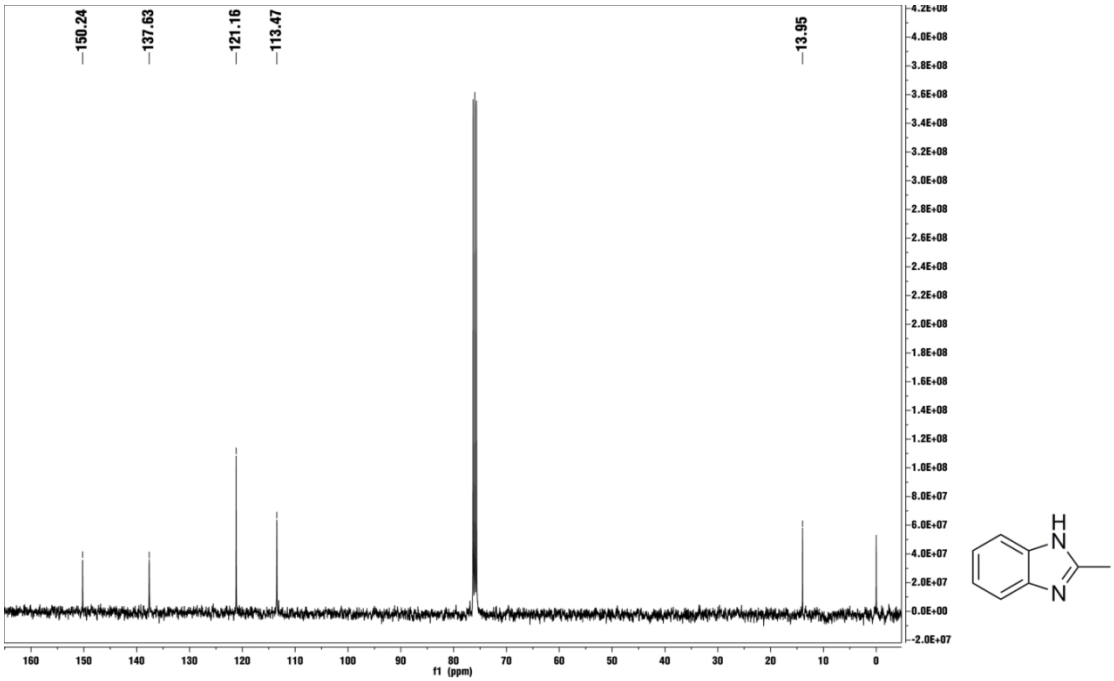


Figure S26. ^{13}C NMR Spectra of 2-Methyl-1H-benzimidazole (2l)

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